Supporting Information

Constructing Highly-Sensitive Ratiometric Nanothermometer Based on Indirect Thermally Coupled Levels

Yubin Wang[a], Lei Lei[a], Enyang Liu[a], Yao Cheng*,[b] Shiqing Xu[a]*

Experimental

1. Synthesis Materials

All chemicals were of analytical grade and were used as received without further purification. Deionized water was used throughout. Erbium acetate hydrate ($Er(Ac)_3 \cdot xH_2O$, 99.9%), ytterbium acetate tetrahydrate ($Yb(Ac)_3 \cdot 4H2O$, 99.9%), yttrium acetate hydrate ($Y(Ac)_3 \cdot xH_2O$, 99.9%), sodium acetate ($NaAc \cdot 3H_2O$, 99.995%), ammonium fluoride (NH_4F, ≥98%), 1-octadecene (ODE, 90%) and oleic acid (OA, 90%) were supplied by Sigma Aldrich Company. Cyclohexane, methanol and absolute ethanol were purchased from Sinopharm Chemical Reagent Company.

2. Synthesis of $NaErF_4$:10Yb core NPs.

$Er(Ac)_3$ (0.72 mmol), $Yb(Ac)_3$ (0.08mmol) and NaAc (0.8 mmol) ware added into a 50 mL three-necked bottle containing 8 mL OA. The mixture was heated at 155 ºC for 30 min to remove water from the solution. Then 12 mL ODE was quickly added to the above solution and the resulted mixture was heated at 150 ºC for another 30 min to form a clear solution, and then cooled down to room temperature. Afterwards, 8 mL methanol solution containing NH^4F (3 mmol) was added and the solution was stirred at 60 ºC for 30 min. After the methanol was evaporated, the solution was further heated at 290 ºC under N_2 for 120 min and then cooled down to room temperature.

The products were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol for three times, and finally re-dispersed in 4 mL cyclohexane.

3. Synthesis of $NaErF_4$:10Yb@$NaYF_4$ core-shell NPs.

$Y(Ac)_3$ (0.8 mmol) and NaAc (0.8 mmol) was added into a 50 mL three-necked bottle containing OA (8 mL). The mixture was heated at 150 ºC for 30 min to remove water from the solution. A solution of ODE (12 mL) was then quickly added and the resulted mixture was heated at 150 oC for another 30 min to form a clear solution, and then cooled down to 80 ºC. Thereafter, the pre-prepared NaErF4:10Yb core NCs in 2 mL cyclohexane was added to the above solution and kept at 110 ºC for 40 min. After the removal of cyclohexane, 8 mL methanol solution containing NH_4F (3 mmol) was added and the solution was stirred at 60 ºC for 30 min. After the methanol was evaporated, the solution was further heated at 290 ºC under N_2 for 120 min, and finally cooled down to room temperature.

4.Characterizations

The X-ray diffraction (XRD) patterns of the samples were recorded by Bruker D8 Advance X-ray diffraction using Cu-Kα (1.5405Å) radiation. The morphologies of the products were studied using an FEI Tecnai G2 F20 S-WTINE transmission electron microscope (TEM, operated at 200kV). Energy dispersive X-ray spectroscope (EDS)-mapping analysis was performed by JEM ARM200F at 200 kV. TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the products on the surface of a carbon coated copper grid. Photoluminescence properties were recorded on a PL3-211-P spectrometer (HORIBA JOBIN YVON, America) assembled with xenon lamp (450 W). Fourier Transform Infrared (FTIR) spectra of the NCs were measured on a Nicolet FTIR spectrometer using the KBr method.

Table S1. Comparison of temperature sensitivities of different reported thermally coupled levels based temperature sensing probes.

Materials	Temperature range (K)	S_a-max(K^{-1})	S_r-max(%K^{-1})	Ref.
$YVO_4:Nd^{3+}@SiO_2$	299-331	0.0021	0.4	S1
Dy-MOF	298-473	0.000785	0.42	S2
$CaWO_4:Yb^{3+},Ho^{3+}$	300-690	0.0205	0.5	S3
$NaYF_4:Yb^{3+}$, Nd^{3+} GC	323-573	0.002	1.05	S4
$ZnO–CaTiO_3:Yb^{3+},Er^{3+}$	300-700	0.0105	1.16	S5
$Sr_2YF_7:Yb^{3+},Tm^{3+}$ GC	303-663	0.003	1.16	S6
$NaYF_4:Yb^{3+},Er^{3+}$	160-300	/	1.20	S7
$NaBiF_4:Yb^{3+},Er^{3+}$	303-483	0.0057	1.24	S8
$BaMoO_4:Tm^{3+},Yb^{3+}$	298-498	0.103	1.36	S9
$Ca_3La_6Si_6O_{24}:Yb^{3+},Er^{3+}$	293-573	0.00391	1.4	S10
$BiVO_4:Yb^{3+},Er^{3+}$	298-873	0.00612	1.58	S11
$NaYbF_4:Tm^{3+}$	298-778	0.0002	1.8	S12
$Ba_3La(PO_4)_3:Yb^{3+},Tm^{3+}$	303-503	0.000131	2.11	S13
$NaErF_4$:10Yb@$NaYF_4$	295-393	0.039	3.76	This work

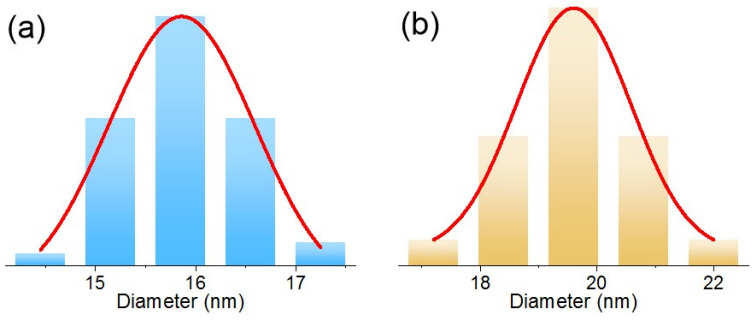

Fig. S1. Size distributions of the as-prepared NaErF4:10Yb core (a) and NaErF4:10Yb@NaYF4 core/shell NPs (b).

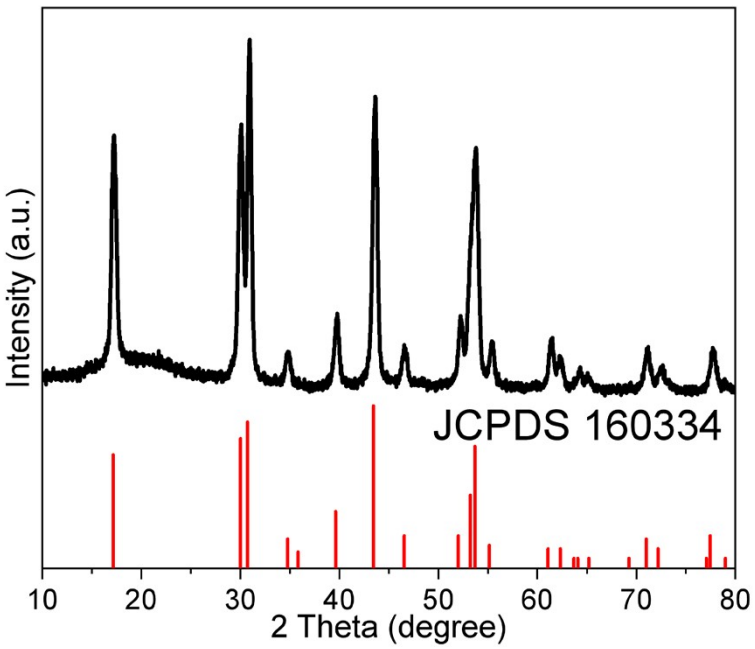

Fig. S2. XRD pattern of the $NaErF_4$:10Yb@$NaYF_4$ core/shell NPs.

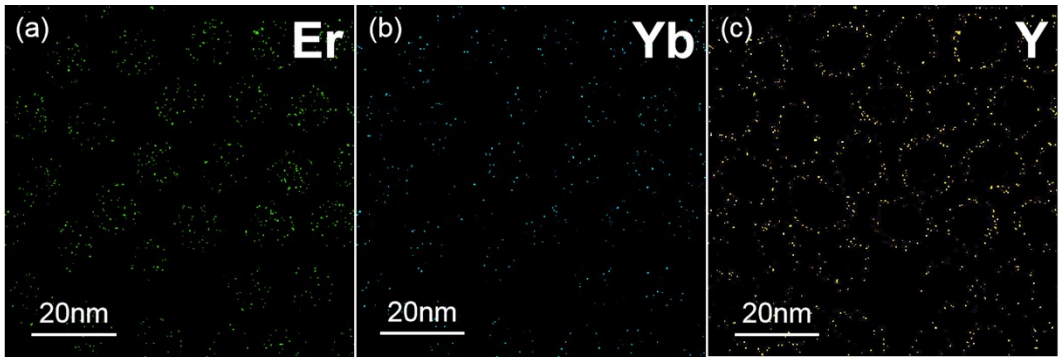

Fig. S3. EDS mapping results of Er (a), Yb (b) and Y (c) elements of the $NaErF_4$:10Yb@$NaYF_4$ NCs.

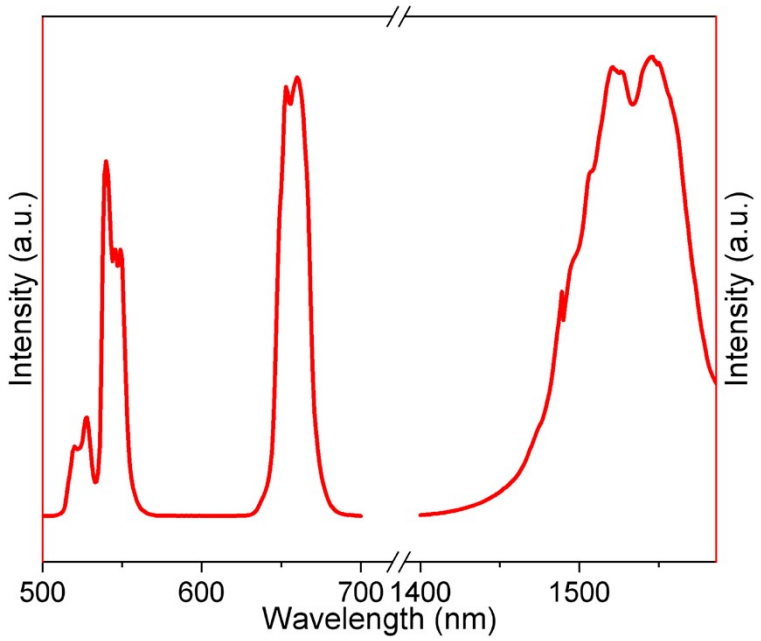

Fig. S4. $NaErF_4$:10Yb@$NaYF_4$ core/shell NCs under 980 nm laser excitation at room temperature.

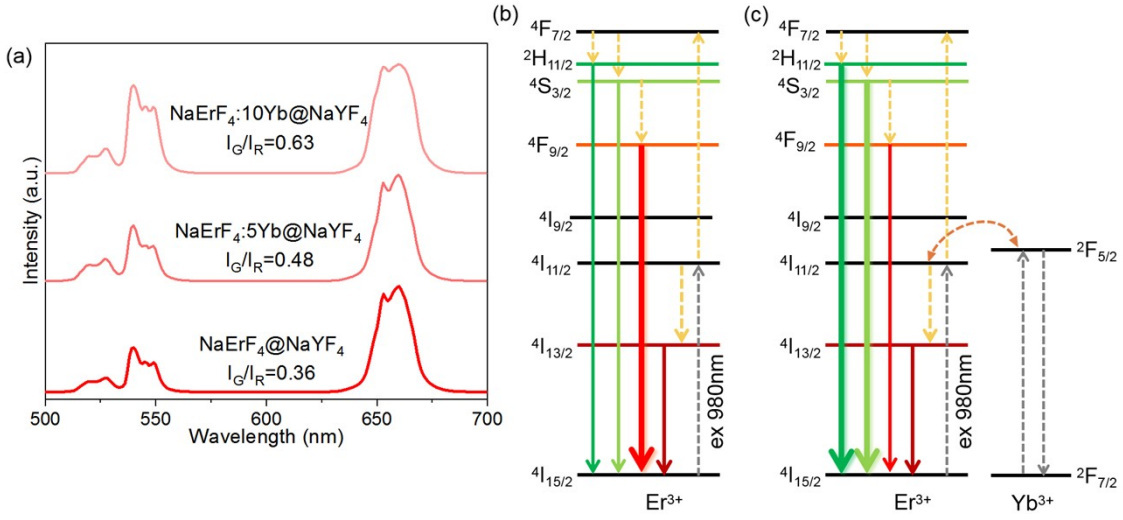

Fig. S5. UC emission spectra of the $NaErF_4$:Yb@$NaYF_4$ NCs with different Yb^{3+} doping content under 980 nm laser excitation (a). Proposed energy transfer processes for the $NaErF_4$@$NaYF_4$ (b) and $NaErF_4$:10Yb@$NaYF_4$ (c) NCs under 980 nm laser excitation.

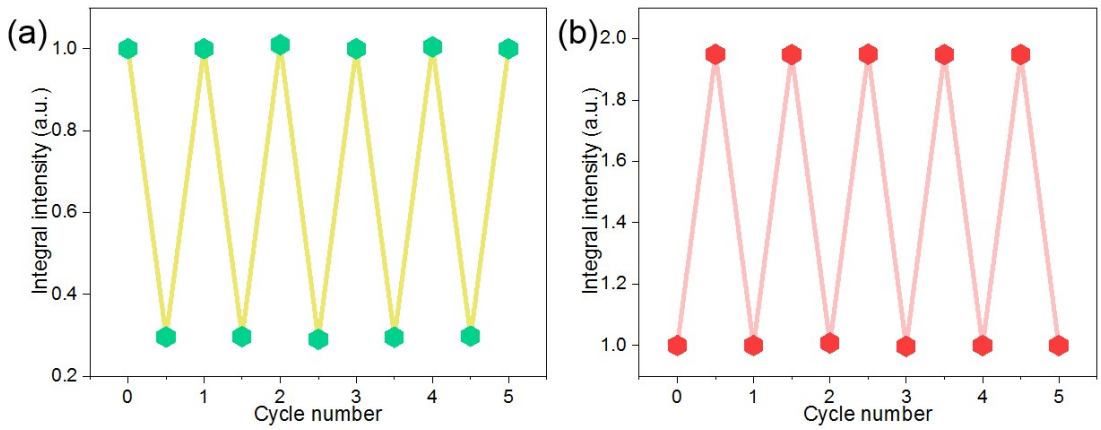

Fig. S6 Repeated integrated emission intensity variations of the 540 nm (a) and 1527 nm (b) in $NaErF_4$: 10Yb@$NaYF_4$ core/shell NCs at 293K and 393K.

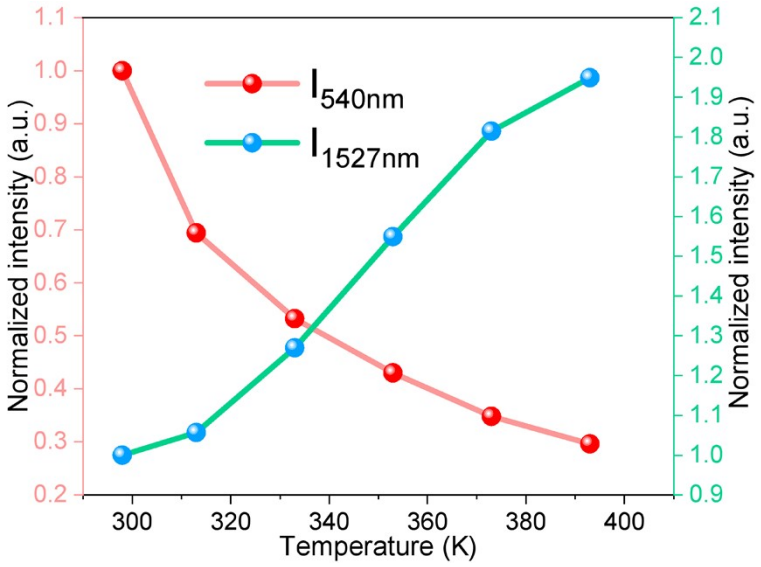

Fig. S7. Normalized integral emission intensity variations vs temperature under 808nm.

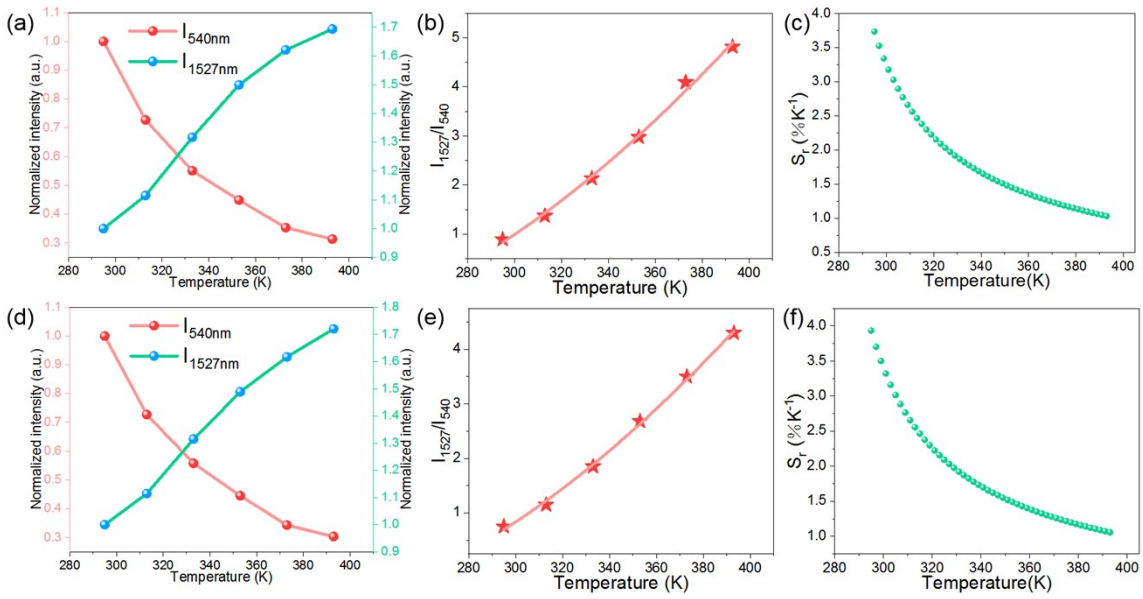

Fig. S8. Temperature-dependent integral emission intensity variations (a), FIR of I_{1527} to I_{540} versus temperature (b), calculated S_r (c) of the $NaErF_4$@$NaYF_4$ NCs. Temperature-dependent integral emission intensity variations (d), FIR of I_{1527} to I_{540} versus temperature (e), calculated S_r (f) of the $NaErF_4$: 5Yb@$NaYF_4$ NCs.

REFERENCES

(1) Kolesnikov, I.E.; Kurochkin, M.A.; Kalinichev, A.A.; Mamonova, D.V.; Kolesnikov, E. Yu.; Kurochkin, A.V.; Lähderanta, E.; Mikhailov, M.D. Effect of Silica Coating on Luminescence and Temperature Sensing Properties of Nd^{3+} Doped Nanoparticles. *J. Alloys Compd.* **2018**, *734*, 136-143.

(2) Xia, T.; Cui, Y.; Yu, Y.; Qian, G. A Luminescent Ratiometric Thermometer Based on Thermally Coupled Levels of Dy-MOF. *J. Mater. Chem. C* **2017**, *5*, 5044-5047.

(3) Xu, W.; Zhao, H.;Li, Y.; Zheng, L.; Zhang, Z.; Cao, W. Optical Temperature Sensing through the Upconversion Luminescence from Ho^{3+}/Yb^{3+} Codoped $CaWO_4$. *Sens. Actuators B Chem.* **2013**, *188*, 1096-1100.

(4) Cai, Z.;Kang, S.; Huang, X.;Song, X.; Xiao, X.; Qiu, J.; Dong, G. Novel Wide Temperature Range and Multi-Mode Optical Thermometry Based on Bi-Functional Nanocrystals-Doped Glass Ceramics. *J. Mater. Chem. C* **2018**, *6*, 9932-9940.

(5) Tiwari,S. P.; Mahata, M. K.; Kumar, K.; Rai, V. K. Enhanced Temperature Sensing Response of Upconversion Luminescence in ZnO-$CaTiO_3$: Er^{3+}/Yb^{3+} Nano-Composite Phosphor. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2015**, *150*, 623–630.

(6) Chen, W.; Hu, F.; Wei, R.; Zeng, Q.; Chen, L.; Guo, H. Optical Thermometry Based on Up-Conversion Luminescence of Tm^{3+} Doped Transparent Sr_2YF_7 Glass Ceramics. *J. Lumin.* **2017**, *192*, 303-309.

(7) Zhou, S.; Deng, K.; Wei, X.; Jiang, G.; Duan, C.; Chen, Y.; Yin, M. Upconversion Luminescence of $NaYF_4$:Yb^{3+}, Er^{3+} for Temperature Sensing. *Opt. Commun.* **2013**, *291*, 138–142.

(8) Du, P.; Luo, L.; Huang, X.; Yu, J. S. Ultrafast Synthesis of Bifunctional Er^{3+}/Yb^{3+} -Codoped $NaBiF_4$ Upconverting Nanoparticles for Nanothermometer and Optical Heater. *J. Colloid Interface Sci.* **2018**, *514*, 172-181.

(9) Liu, X.; Lei, R.; Li,Y.; Xu, S. Tm^{3+}/Yb^{3+}:$BaMoO_4$ Phosphor for High-Performance Thermometry Operating in the First Biological Window. *Opt. Lett.* **2019**, *44*, 3633.

(10) Zhang, J.; Hua, Z. Effect of Dopant Contents on Upconversion Luminescence and Temperature Sensing Behavior in $Ca_3La_6Si_6O_{24}$:Yb^{3+}-Er^{3+}/Ho^{3+} Phosphors. *J. Lumin.* **2018**, *201*, 217–223.

(11) Kshetri, Y. K.; Regmi, C.; Chaudhary, B.; Kim, H.-S.; Kim, T.-H.;Rosei, F.; Lee, S. W. $BiVO_4$ Ceramics for High-Sensitivity and High-Temperature Optical Thermometry. *J. Lumin.* **202**0, *230*, 117739.

(12) Du,P.; Luo, L.; Yu, J. S. Controlled Synthesis and Upconversion Luminescence of Tm^{3+}-Doped $NaYbF_4$ Nanoparticles for Non-Invasion Optical Thermometry. *J. Alloy. Compd.* **2018**, *739*, 926–933.

(13) Cao, J.; Zhang, J.; Li, X. Upconversion Luminescence of $Ba_3La(PO_4)_3$: Yb^{3+}-Er^{3+}/Tm^{3+} Phosphors for Optimal Temperature Sensing. *Appl Opt.* **2018**, *57*, 1345–1350